

Patent

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Shinji INAZAWA et al.

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Examiner: YANG, JIE

For: METHOD OF PRODUCING FINE METAL POWDER

Assistant commissioner for Patents

Washington, DC 20231

Sir:

**RULE 132 DECLARATION**

I, Keiji KOYAMA do here by declare the followings:

I am a citizen of Japan, living in Higashiimazato 3-19-14,  
Higashinari-Ku, Osaka-Shi, Osaka 573-0011, Japan;

I graduated from Material and Life Science, Graduate  
School of Engineering, Osaka University in 1998;

I have been employed by SUMITOMO ELECTRIC INDUSTRIES, LTD.  
since 1998, and now engage in the study of the circuit connection  
technique at Electronics & Materials R & D Laboratories.

I am one of co-inventors of the invention which is  
disclosed and claimed in the present application. I know the  
Final Office Action on February 5, 2008 and the Advisory Action  
on May 15, 2008 were issued for the present invention noticing  
that the invention claimed in the subject application was  
rejected under 35 U.S.C. § 103 as being unpatentable over  
Puetter (DE'865) in view of Senda et al. (US'830) and Harrison  
et al. (US'581).

Further, I know in this Advisory Action, the Examiner pointed out that the present five data shown in Fig. 1 alone are not sufficient for evidencing the difference between (1) the relation between the ratio of trivalent titanium ions and tetravalent titanium ions and the particle diameter of a fine metal powder and (2) the relation between the concentration of trivalent titanium ions alone and the above particle diameter.

Therefore, following Experiments 1 and 2 were performed by myself or under my supervision in order to add the data clarifying the difference between the above relations (1) and (2).

<<Experiment 1>>

<Sample 1-1 to 1-9>

[Preparation of Reducing Agent Solution]

A 20 % hydrochloric acid solution of titanium tetrachloride was prepared. The amount of the titanium tetrachloride was set such that when a reducing agent solution obtained by subjecting the solution to cathode electrolytic treatment in the subsequent step was mixed with a reaction solution, described in the following item, at a predetermined ratio, and a pH adjuster or ion exchanged water, as required, was added to produce a predetermined amount of mixed solution, the molar ratio of the sum of trivalent and tetravalent titanium ions to the total amount of the mixed solution would be 0.2 M (mole/liter). The pH of the solution was 4.

The solution was then poured into one of cells in a two-cell type electrolytic cell divided by an anion exchange membrane produced by Asahi Glass Co., Ltd. Further, a sodium

sulfate solution having a molar ratio of 0.1 M was poured into the other cell.

Eight types of reducing agent solutions in which tetravalent titanium ions were reduced to trivalent titanium ions at the respective ratios shown in Table 1 were prepared by dipping carbon felt electrodes in the solution, and carrying a 3.5 V DC current under constant-voltage control between the electrodes, the electrode dipped in the solution of titanium tetrachloride used as a cathode and the electrode dipped in the sodium sulfate solution used as an anode (Sample 1-2 to 1-9). Further, an aqueous solution in which an anode electrolytic treatment was not performed (that is, the proportion of trivalent titanium ions was 0 %) was also prepared for comparison (Sample 1-1).

#### [Production of Reaction Solution]

Nickel chloride and trisodium citrate were dissolved in ion exchanged water, to produce a reaction solution. The amount of the nickel chloride was set such that the molar ratio thereof to the total amount of the mixed solution would be still 0.16 M. The amount of the trisodium citrate was adjusted such that the molar ratio thereof to the total amount of the mixed solution would be 0.3 M.

#### [Production of Fine Metal Powder]

One of the above nine types of the reducing agent solutions was poured into a reaction cell, and was agitated while maintaining the liquid temperature thereof at 50 °C, a saturated solution of sodium carbonate serving as a pH adjuster was added

to the solution to adjust the pH of the solution to 5.2, the reaction solution was gradually added to the solution, and ion exchanged water was further added thereto as required, to produce a predetermined amount of mixed solution. The reaction solution and the ion exchanged water, which have been previously warmed to 50 °C, were added.

When the mixed solution continued to be agitated for several minutes while maintaining the liquid temperature thereof at 50 °C, sediments were deposited in each of Sample 1-2 to 1-9. Accordingly, the agitation was stopped, to immediately filter, rinse, and dry the sediments, to obtain fine powders (nickel fine powders). The pH of the mixed solution at the time point where the reaction was terminated was 4.0. Almost all of the titanium ions in the mixed solution were tetravalent. Further, sediments were not deposited in Sample 1-1, not to obtain fine metal powders.

[Measurement of average particle diameter]

The appearances of the obtained fine metal powders were photographed using a scanning-type electron microscope. When the particle diameters of all the fine metal powders whose actual sizes fall within a rectangular shape area of  $1.8\text{ }\mu\text{m} \times 2.4\text{ }\mu\text{m}$  of the photograph were measured and averaged. The results are shown in Table 1. Further, the relation between the mole % of trivalent titanium ions in the reducing agent solution and the average particle diameter (nm) of the fine metal powders is shown in Fig. 1.

TABLE 1

Sample	Concentration of Ti Ions (Mole %)		Average Particle Diameter of Fine Metal Powder (nm)
	Trivalent	Tetravalent	
1-1	0	100	0
1-2	10	90	20
1-3	25	75	100
1-4	35	65	200
1-5	45	55	300
1-6	65	35	400
1-7	80	20	450
1-8	90	10	460
1-9	100	0	470

FIG. 1

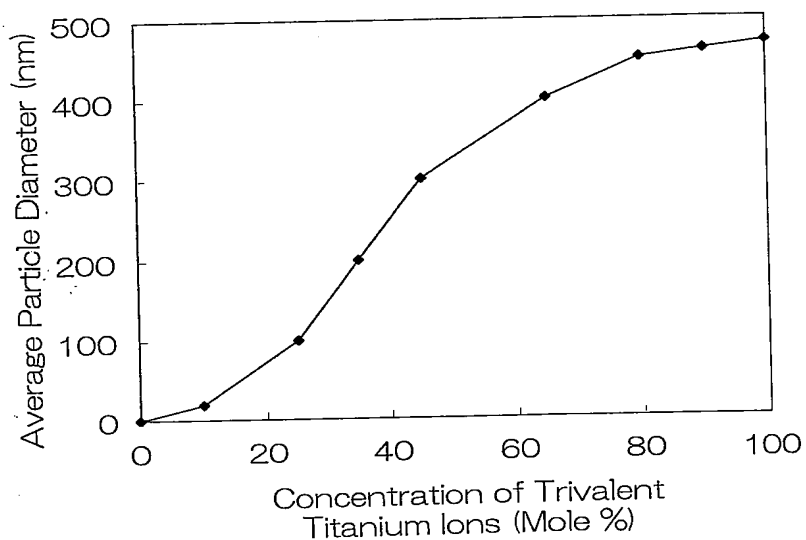


Table 1 and Fig. 1 confirm that a particle diameter of a produced fine metal powder can be changed by making trivalent titanium ions and tetravalent titanium ions coexist in a mixed

solution serving as a reaction system, and by adjusting a molar ratio between both the ions.

<<Experiment 2>>

Comparative Example 2 in the present specification which was performed as a repetition of Example 5 of US'830 was performed again.

[Comparative Example 2]

Nickel Chloride, nitorilotrisodium triacetate, and trisodium citrate were dissolved in ion exchanged water, to produce a solution.

A 25 % ammonia solution was then added to the solution to adjust the pH thereof to 10.5, and was then agitated while maintaining the liquid temperature thereof at 50 °C, and a 20 % hydrochloric acid solution of titanium trichloride was poured thereinto using an injection syringe such that it does not come in contact with outward air in a nitrogen gas current, to produce a predetermined amount of mixed solution.

The molar ratio of each of components to the total amount of the mixed solution was 0.04 M of the nickel chloride, 0.1 M of the nitorilotrisodium triacetate, 0.1 M of the trisodium citrate, and 0.04 M of the titanium trichloride.

The moment the solution of titanium trichloride was poured, a part of the solution became clouded. When the white clouding subsided after several minutes, however, segments in two colors, i.e., white segments and black segments stacked thereon were obtained. The pH of the solution was raised to 2.0.

The segments in two colors were separately extracted, and were respectively rinsed and dried, to obtain fine powders in two colors, i.e., white and black.

When the composition of the white fine powder was actually measured by ICP emission spectrometry, it was titanium oxide. When the amount thereof was weighed, it was confirmed that approximately 20 % of titanium ions added to the solution were deposited as titanium oxide.

On the other hand, it was confirmed that the black fine powder was nickel having a purity of 92 %.

The average particle diameter of the fine metal powders was 800 nm (0.8  $\mu$ m) when it was measured in the same manner as described above.

[Sample 2-1 to 2-6]

An experiment was performed in the same manner as above Comparative Example 2 except that the molar ratio ( $M =$  mole/liter) of the above titanium trichloride to the total amount of the mixed solution was set to the values shown in Table 2 by adjusting the poured amount of the solution of titanium trichloride. Then, segments in two colors, i.e., white segments and black segments stacked thereon were obtained in each of Sample 2-2 to 2-6 as in the case of Comparative Example 2. On the other hand, segments were not obtained in Sample 2-1 in which a solution of titanium trichloride was not poured.

The black segments obtained in respective Sample were recovered, washed and dried to obtain fine metal powders, and their average particle diameters were measured in the above-described manner. Then, all of them were 800 nm and

constant.

The above results are shown in Table 2 and Fig. 2.

TABLE 2

Sample	Concentration of Trivalent Ti Ions (M)	Average Particle Diameter of Fine Metal Powder (nm)
2-1	0	0
2-2	0.01	800
2-3	0.02	800
2-4	0.03	800
Comparative Example 2	0.04	800
2-6	0.06	800
2-7	0.10	800

FIG. 2

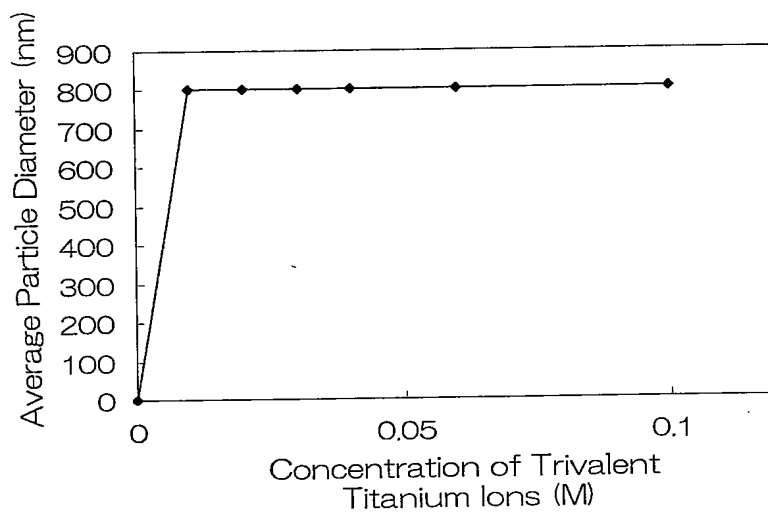


Table 2 and Fig. 2 clearly shows that when only trivalent titanium ions are contained in a mixed solution serving as a reaction system, a particle diameter of a produced fine metal particle cannot be changed even if its concentration is



adjusted.

#### <<Conclusion>>

The results of Experiment 1 confirm that according to the producing method of the present invention in which trivalent titanium ions and tetravalent titanium ions coexist in a reaction system, a particle diameter of a produced fine metal powder can be changed according a molar ratio between both the titanium ions by adjusting this molar ratio, and therefore, a fine metal powder having a certain particle diameter can be produced with a good reproducibility by intentionally adjusting a molar ratio between both the ions.

Contrary to this, according to the producing method of US'830 in which trivalent titanium ions alone are contained in a reaction system, even when the concentration (M) of the above trivalent titanium ions is changed, a particle diameter of a produced fine metal powder cannot be changed and is always constant. This result is different from the anticipation which I and the other co-inventors of the present invention initially had. We think this is due to the following reason.

That is, as described in the present specification, according to the producing method of the present invention in which trivalent titanium ions and tetravalent titanium ions coexist in a reaction system, a fine metal powder is formed while the function of reducing and depositing ions of a metal element by trivalent titanium ions to make a fine metal powder grow and the function of restraining the growth of a fine metal powder by the tetravalent titanium ions exert on the same fine metal powder. Therefore, since a reducing agent solution in which

a ratio of both the ions is previously adjusted is mixed to a reaction solution containing metal ions to start reaction, the contradictory functions of the respective ions can be adjusted in their intensities, whereby an average particle diameter of a produced fine metal powder can be controlled optionally.

On the other hand, according to the producing method of US'830 in which trivalent titanium ions alone are contained in a reaction system, an oxidation-reduction potential between the above trivalent titanium ions and metal ions to be deposited is constant even when the concentration thereof is changed. Moreover, since the reaction is instantly finished as described in Experiment 2, tetravalent titanium ions produced by the reaction do not influence the particle diameter of a fine metal powder. Consequently, even when the concentration of trivalent titanium ions is changed, a deposited amount of a fine metal powder is merely changed, and its particle diameter is not changed.

Date: June.25, 2008

By: Keiji Koyama  
Keiji KOYAMA